

# Thermoelectric properties of two-dimensional slabs of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ from first principles

Deepa Kasinathan,<sup>1</sup> Vicente Pacheco-Espejel,<sup>2</sup> and Helge Rosner,<sup>1</sup>

<sup>1</sup>*Max-Planck-Institut für Chemische Physik fester Stoffe, 01187 Dresden, Germany and*

<sup>2</sup>*Fraunhofer Institut für Fertigungstechnik und Angewandte Material Forschung, Institutsteil Dresden, Germany*

Thermoelectric effects enable the direct conversion between thermal and electrical energy and provide an alternative route for power generation and refrigeration. The clathrate  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  has the highest figure of merit ( $ZT \approx 1$ ) among other members in the family of type-I inorganic clathrates. Enhancement of the thermoelectric properties have been observed in multilayered superlattices, quantum wires and in nanostructured materials, either due to the increase in power-factor ( $S^2\sigma$ ) or due to the reduction of lattice thermal conductivity ( $\kappa$ ). Here, we investigate the thermoelectric properties of two-dimensional slabs with varying thickness of  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  using semi-classical Boltzmann transport theory with constant scattering approximation. We observe that, there exists a delicate balance between the electrical conductivity and the electronic part of the thermal conductivity in reduced dimensions and the insights from these results can directly be used to control particle size in nanostructuring experiments. The calculated properties are consistent with the recent, first measurements on bulk nanostructured samples.

## I. INTRODUCTION

Thermoelectric power generators use the temperature gradient to drive the charge carriers (electrons and holes) from one end of the material to the other, thereby creating a potential difference. This provides the means of converting the temperature gradient directly into electricity without the need for any moving parts. However, the inherent low efficiency of the prevailing materials is inadequate to compete with the conventional power generation and refrigeration. Hence the central issue in thermoelectrics research is to increase the thermoelectric figure of merit  $ZT$ , a dimensionless quantity defined as  $ZT = (S^2\sigma/\kappa)/T$ , where  $S$  is the Seebeck coefficient (also known as thermopower),  $\sigma$  is the carrier conductivity,  $\kappa$  is the total thermal conductivity ( $= \kappa^{el}$  (electron) +  $\kappa^{ph}$  (phonon)), and  $T$  is the absolute temperature. As these transport properties depend on interrelated material characteristics, finding thermoelectric materials with enhanced  $ZT$  values remains a challenging issue. To enable a more widespread usage of thermoelectric technology power generation and heating/cooling applications,  $ZT$  of at least 2-3 is required. Two different research approaches have been proposed for developing the next generation of thermoelectric materials: (i) investigating new families of advanced bulk thermoelectric materials, and (ii) studying low-dimensional or nanostructured material systems. The increase in  $ZT$  of nanostructured materials could either be from the reduction of  $\kappa^{ph}$  or from the enhancement of the power factor,  $S^2\sigma$ . Hence, a microscopic picture of the transport properties and its response to nanostructuring is necessary to fine tune the preparation techniques.

Type-I inorganic clathrates are host-guest structures with the guest atoms trapped in the framework of the host structure. From a thermoelectric point of view, the clathrates are interesting because they are semiconductors with adjustable bandgaps. Investigations in the past

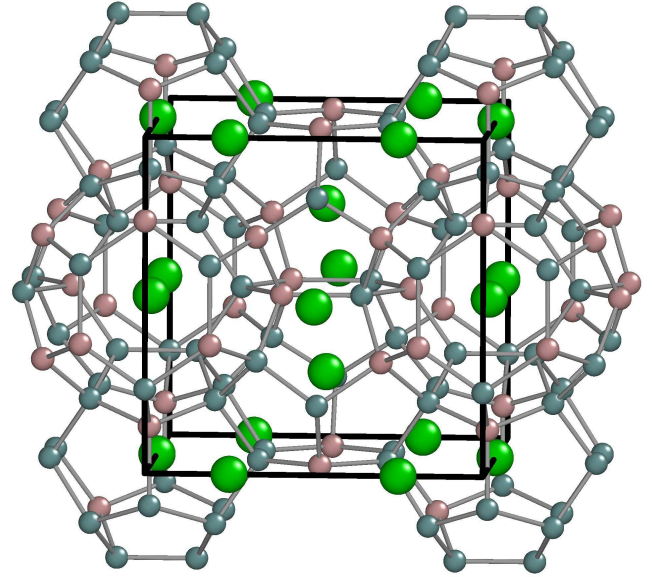


FIG. 1. (Color online) The crystal structure of type-I clathrate  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ . The large (green) atoms at the center of the cages are the Ba atoms. The framework is made up of two kind of cages: a 20-atom smaller pentagonal dodecahedron and a 24-atom larger tetrakaidecahedron. The brown atoms are Ga and the grey atoms are Ge.

decade have shown that type-I clathrates  $A_8\text{Ga}_{16}\text{Ge}_{30}$  ( $A = \text{Ba}, \text{Sr}, \text{Eu}$ ) may have the unusual property of "phonon glass-electron crystal" proposed by Slack for good thermoelectric materials.<sup>1,2</sup> Among the known inorganic clathrates,  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  has the highest figure of merit ( $ZT \approx 1$ ). Recently, first successful attempts have been made to synthesize nanostructures of  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  using the bottom-up approach.<sup>3</sup> The nanoparticles contained mainly thin plates that were indexed according to the [100] direction of the clathrate structure type. The

measured Seebeck coefficient reaches  $-145 \mu\text{V/K}$  at 648 K, though the  $ZT$  values are quite low (0.02) due to the low sample density. Motivated by these measurements, in our work, we concentrate on obtaining a microscopic picture of the electronic contributions to the thermoelectric properties for reduced dimensions. In particular, we have considered two-dimensional slabs of varying thickness with the [100] surface termination and calculated the thermoelectric properties using the semi-classical Boltzmann transport theory. We observe that, there exists a delicate balance between the electrical conductivity and the electronic part of the thermal conductivity in reduced dimensions and insights from these results can directly be used to control particle size in nanostructuring experiments.

## II. STRUCTURE

The type-I  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  clathrate has a cubic crystal structure with the space group  $Pm\bar{3}n$ . The crystal structure contains 46 tetrahedrally coordinated host atoms (Ga/Ge) which make two small dodecahedron cages and six larger tetrakaidecahedral cages (Fig. 1). The heavy guest atoms (Ba) were placed at the center of the cages (Wyckoff positions  $2a$  and  $6d$ ). The Ga atoms were distributed in the framework with twelve Ga atoms at  $24k$ , one Ga at  $16i$  and three Ga at  $6c$  sites, resulting in only seven short Ga-Ga bonds with a bond length of  $\approx 2.48 \text{ \AA}$ . Such a distribution of the Ga atoms was done to accommodate the Ga-Ga bond avoidance observed experimentally. The remainder of the framework positions were then filled with Ge atoms. The symmetry setting for the calculations was thus lowered to space group 1 to accommodate such a random distribution of Ga/Ge atoms.

## III. CALCULATIONAL DETAILS

Non-spin-polarized DFT total energy and Kohn-Sham band-structure calculations were performed applying the full-potential local-orbital code (version FPLO9.01.35), within the local density approximation (LDA).<sup>4,5</sup> The Perdew and Wang flavor<sup>6</sup> of the exchange correlation potential was chosen for the scalar relativistic calculations. The calculations were carefully converged with respect to the number of  $k$  points. The transport properties were calculated using the semiclassical Boltzmann transport theory<sup>7-9</sup> within the constant scattering approximation as implemented in BoltzTraP.<sup>10</sup> This approximation is based on the assumption that the scattering time  $\tau$  determining the electrical conductivity does not vary strongly with energy on the scale of  $kT$ . Additionally, no further assumptions are made on the dependence of  $\tau$  due to strong doping and temperature. This method has been successfully applied to many narrow band gap materials including clathrates and as well as to oxides.<sup>9,11-13</sup> One main concern when calculating trans-

port coefficients, is the underestimation of band gaps using the standard DFT functionals. Such an underestimation of band gaps manifests in the reduction of thermopower at higher temperatures due to bipolar conduction. To overcome this problem, we concentrate on analyzing the trend in the calculated thermopower for various concentrations of electron and hole doping rather than quantifying them.

## IV. RESULTS

As mentioned previously, the nanoparticles of  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  synthesized recently contained mainly nano-plates oriented along [100] direction. Therefore, we begin by considering a three-layer slab with a [100] surface termination and calculate the thermoelectric properties. Due to the complex nature of the crystal structure of the clathrates, there is no obvious cleavage plane to choose from when creating the slab geometries. Moreover, the cages are all interconnected and every choice of termination will destruct the cage network. Hence, we calculated the thermoelectric properties of many three-layer slabs with different [100] surfaces. Comparing the values of Seebeck coefficient for the various calculations, we have identified the termination which results in increasing thermopower as a function of temperature. Having identified an advantageous slab geometry, we proceeded to increase the thickness of the slabs and evaluated the thermoelectric properties without changing any other structural parameters. Collected in Fig. 2 are the Seebeck coefficient, electrical conductivity and the electronic part of the thermal conductivity as a function of the chemical potential for a three, four and five layer slab for various temperatures. The thermoelectric properties of the bulk system is also plotted alongside for easy comparison. The bulk system is a Zintl phase and hence a semiconductor. This results in purely electron (chemical potential  $\mu > 0$ ,  $S$  is negative) or hole (chemical potential  $\mu < 0$ ,  $S$  is positive) conductivity for low carrier concentrations. On the contrary, the slab geometries no longer retain the Zintl composition at the surface and hence show multiband behavior, witnessed by the change in sign of  $S$  for a given  $\mu$ .

The values of the calculated thermopower are not affected by the constant scattering time approximation used to calculate the various transport properties, since the expression for  $S$  is independent of  $\tau$ . This means that  $S$  is directly dependent on the electronic structure of the material. For the three-layer slab, at  $\mu = 1.2 \text{ eV}$ , the charge carriers are mainly electrons and  $S$  is increasing with temperature and reaches a value of  $-90 \mu\text{V/K}$  at 1100 K. Upon increasing the thickness of the slab to four layers, the trend in  $S$  is similar and at  $\mu = 1.2 \text{ eV}$ , it reaches  $-110 \mu\text{V/K}$  at 1100 K. Adding an additional layer retains the large values of thermopower. Comparing this to the bulk, we can conclude that  $S$  remains unaffected (even slightly enhanced) upon lowering the

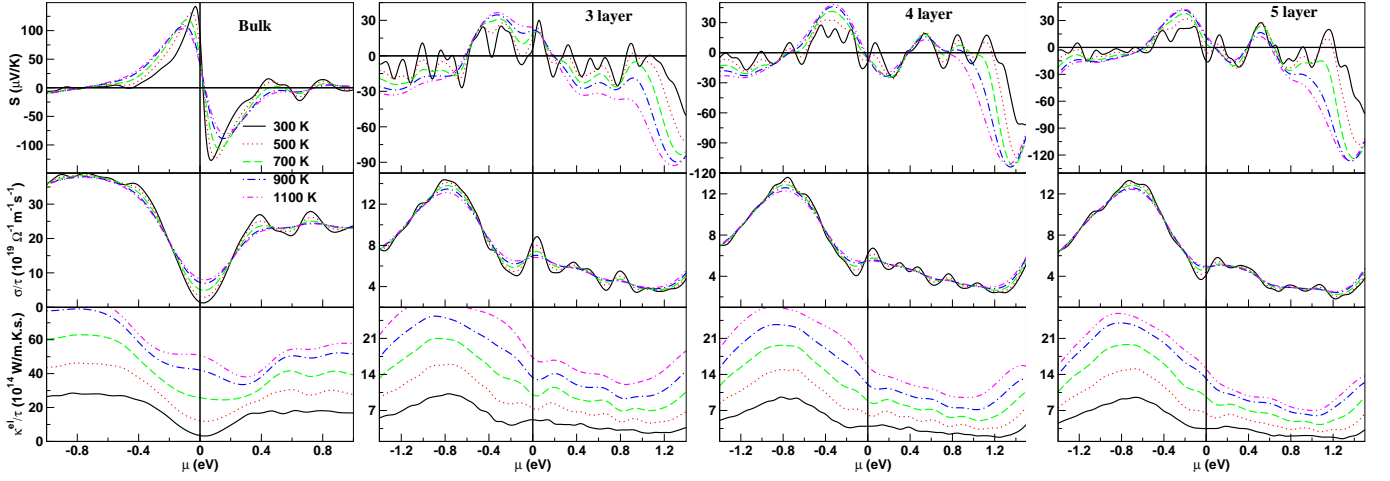


FIG. 2. (Color online) Temperature dependence of the calculated thermoelectric properties  $S$ ,  $\sigma/\tau$ , and  $\kappa^{el}/\tau$  as a function of the chemical potential for bulk  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  along with  $[100]$  terminated slabs of varying thickness.

dimensions for  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ . On the contrary, the electrical conductivity of the slabs reduced by a factor of two for the slab systems in comparison to the bulk. Interestingly, the electronic part of the thermal conductivity  $\kappa^{el}$  is also reduced with respect to the bulk for the slab geometries. This term goes into the denominator of the expression that defines  $ZT$ , and a lower  $\kappa^{el}$  for the slabs means an increase in  $ZT$  values with respect to the bulk. Assuming that nanostructuring reduces the phononic part of the thermal conductivity  $\kappa^{ph}$  by introducing grain boundaries, one can obtain improved thermoelectric performance in nanostructured  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{16}$  clathrates.

## V. CONCLUSIONS

We have calculated the electronic contribution to the thermoelectric properties for two-dimensional

slabs of  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  clathrate from semi-classical Boltzmann statistics. We discern a dependence of the different surface terminations and slab thickness on the calculated thermoelectric properties. A delicate balance exists between  $S$ ,  $\sigma$  and  $\kappa^{el}$  in reduced dimensions. Enhanced values of  $S$  is obtained for heavily  $n$ -doped slabs of  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  with respect to the bulk. Both  $\sigma$  and  $\kappa^{el}$  are reduced for the slabs in comparison to the bulk, but  $S^2\sigma/\kappa^{el}$  of the slabs are comparable to the best bulk values. Assuming a reduction of  $\kappa^{ph}$  via nanostructuring, one can anticipate improved values of  $ZT$  for low dimensional  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  systems.

**Acknowledgement:** This work was supported by the Deutsche Forschungsgemeinschaft DFG in the frame of a priority program SPP1386 *NanostrukturierteThermoelektrika* : *Theorie,ModellsystemmeundkontrollierteSynthese* with the grant number PA 1821/1-1.

- <sup>1</sup> G. Slack, in *CRC Handbook of Thermoelectrics*, edited by D. M. Rowe (CRC, Boca Raton), 407 (1995).
- <sup>2</sup> G. A. Slack, Mater. Res. Soc. Symp. Proc. **478**, 47 (1997).
- <sup>3</sup> V. Pacheco, R. Cardoso-Gil, D. Kasinathan, H. Rosner, M. Wagner, L. Tepech-Carrillo, W. Carrillo-Cabrera, K. Meier and Yuri Grin, arXiv:1111.3233
- <sup>4</sup> K. Koepnick and H. Eschrig, Phys. Rev. B **59**, 1743 (1999).
- <sup>5</sup> I. Opahle, K. Koepnick, and H. Eschrig, Phys. Rev. B **60**, 14035 (1999).
- <sup>6</sup> J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- <sup>7</sup> J. M. Ziman, *Electrons and Phonons* (Oxford University

- Press, New York, 2001).
- <sup>8</sup> W. Jones and N. H. March, *Theoretical Solid State Physics* (Courier Dover, New York, 1985).
- <sup>9</sup> G. K. H. Madsen, K. Schwarz, P. Blaha, and D. J. Singh, Phys.Rev. B **68**, 125212 (2003).
- <sup>10</sup> G. K. H. Madsen and D. J. Singh, Comput. Phys. Commun. **175**, 67 (2006).
- <sup>11</sup> S. Johnsen, A. Bentien, G. K. H. Madsen, Bo B. Iversen, and M. Nygren, Chem. Mater. **18**, 4633 (2006).
- <sup>12</sup> D. J. Singh and D. Kasinathan, J. Electron. Mater. **36**, 736 (2007).
- <sup>13</sup> H. J. Xiang, and D. J. Singh, Phys. Rev. B **76**, 195111 (2007).